

Description

Palladium and platinum complexes

- 5 Organometallic compounds, especially compounds of the d^8 metals, will find use as functional components in the near future as active components (= functional materials) in a series of different types of application which can be classed within the electronics industry in the broadest sense.

10 The organic electroluminescent devices based on organic components (for a general description of the construction, see US-A-4,539,507 and US-A-5,151,629) and their individual components, the organic light-emitting diodes (OLEDs), have already been introduced onto the market, as demonstrated by the car radios having organic displays from Pioneer. For the polymeric OLEDs (PLEDs) too, a first product in the form of a relatively small display (in a shaver from PHILIPS N.V.) has become available on the market. Further products of this type will shortly be introduced. In spite of this, distinct improvements are still necessary here for these displays to provide real competition to the currently market-leading liquid crystal displays (LCDs) or to overtake them.

25 A development in this direction which has emerged in recent years is the use of organometallic complexes which exhibit phosphorescence instead of fluorescence [M. A. Baldo, S. Lamansky, P. E. Burrows, M. E. Thompson, S. R. Forrest, Applied Physics Letters, 1999, 75, 4-6].

30 For theoretical reasons relating to the spin probability, up to four times the energy efficiency and performance efficiency are possible using organometallic compounds as phosphorescence emitters. Whether this new development will establish itself firstly depends strongly upon whether corresponding device compositions can be found which can utilize

these advantages (triplet emission = phosphorescence compared to single emission = fluorescence) in OLEDs too. The essential conditions for practical use are in particular a long operative lifetime, a high stability
5 against thermal stress and a low use and operating voltage, in order to enable mobile applications.

In addition, there has to be efficient chemical access to the corresponding organometallic compounds. Of particular interest in this context are organopalladium
10 and -platinum compounds. Especially taking into account the cost of palladium and platinum, it is of crucial importance here that efficient access to the corresponding derivatives is enabled.

15 The present invention provides 5'-mono-, 5',5''-di-halo-functionalized mono- and bis-ortho-metallated organopalladium and organoplatinum compounds (according to compounds (1), (1a) or (2), (2a)), 5',5''-mono- or di-halo-functionalized bis-ortho-metallated bridged
20 organopalladium and organoplatinum compounds (according to compound (3) and (4)), and cationic, uncharged or anionic 5'-mono-halo-functionalized mono-ortho-metallated organopalladium and organoplatinum compounds (according to compound (5), (6), (7) and (8)), which
25 will be the central key building blocks for obtaining highly efficient triplet emitters, since the halogen function can be converted to a multitude of functions with the aid of common methods described in the literature. This allows not only the covalent
30 incorporation of these active, light-emitting centers into a multitude of polymers, but also the tailoring of the optoelectronic properties of these building blocks. For instance, starting from the structure mentioned, typical C-C bond-forming reactions (for example Stille or Suzuki coupling), or else C-heteroatom bond-forming
35 reactions (for example, for C-N: Hartwig-Buchwald coupling, similarly also for C-O and C-P) are possible here, in order thus either to further functionalize the halogen-functionalized compounds or to use them as

(co)monomers in the preparation of corresponding polymers.

5' -mono-, 5,5"-di-halo-functionalized mono- and bis-ortho-metalated organopalladium and organoplatinum compounds (according to compounds (1), (1a) or (2), (2a)), 5',5"-mono- or di-halo-functionalized bis-ortho-metalated bridged organopalladium and organoplatinum compounds (according to compound (3) and (4)) and cationic, uncharged or anionic 5'-mono-halo-functionalized mono-ortho-metalated organopalladium and organoplatinum compounds (according to compound (4), (6), (7) and (8)) have not been described to date in the literature, but their efficient preparation and availability as pure materials is of great significance for various electrooptical applications.

The closest prior art may be regarded as being the monobromination and monoiodination of a cationic ruthenium(II) complex which, in addition to the ortho-metalated 2-phenylpyridine ligand, also bears 2,2'-bipyridine ligands [C. Coudret, S. Fraysse, J.-P. Luanay, Chem. Commun., 1998, 663-664]. The brominating agent used is N-bromosuccinimide, the iodinating agent a mixture of iodobenzene diacetate and elemental iodine in a molar ratio of one to one. The isolated yield after chromatographic purification is reported as 95% in the case of bromination, and as 50% in the case of iodination.

The bromination, described by Clark et al., of ortho-metalated 2-phenylquinoline and 2,3-diphenylquinoxaline ligands of ruthenium(II) carbonyl chloro and osmium(II) carbonyl chloro complexes with pyridinium perbromide should also be regarded analogously. After chromatographic purification, yields of from 27% to 92% were obtained [A.M. Clark, C.E.F. Rickard, W.R. Roper, L.J. Wright, J. Organomet. Chem., 2000, 598, 262-275].

In addition, it has been shown in the application

WO 02/068435 that the halogenation of octahedral homo- and heteroleptic rhodium and iridium complexes with an ortho-metalated ligand set proceeds very selectively and in good to very good yields.

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However, this prior art described in the abovementioned references has the following disadvantages:

- (1) only the halogenation of Ru, Os, Rh and Ir complexes, but not that of Pd or Pt compounds, is described.
- (2) no viable teaching is provided as to how square planar, homo- and heteroleptic palladium and platinum complexes with an ortho-metalated ligand set can be halogenated selectively on the coordinated ligand. Rather, it is known that these complexes are readily amenable to oxidative addition by halogens (L. Chassot, E. Müller, A. Zelewsky, Inorg. Chem. 1984, 23, 4249-4253) and thus, according to the prior art, change from square planar to octahedral geometry.

It has now been found that, surprisingly, the novel compounds (1), (1a), (2), (2a), according to scheme 2, are obtained starting from the bis-ortho-metalated organopalladium or organoplatinum compounds (9), (9a), (10), (10a), and that the novel compounds (3) or (4), according to scheme 3, are obtained starting from the bis-ortho-metalated, bridged organopalladium and organoplatinum compounds (11) or (12), and that the novel compounds (5), (6), (7) or (8), according to scheme 4, are obtained starting from the cationic, uncharged or anionic functionalized mono-ortho-metalated organopalladium and organoplatinum compounds (13), (14), (15) and (16) with a halogen or interhalogen, optionally in the presence of a base and optionally of a Lewis acid, and in the presence or with subsequent addition of a reducing agent or of an organic N-halogen compound, optionally in the presence of a Brønsted acid, and in the presence or with

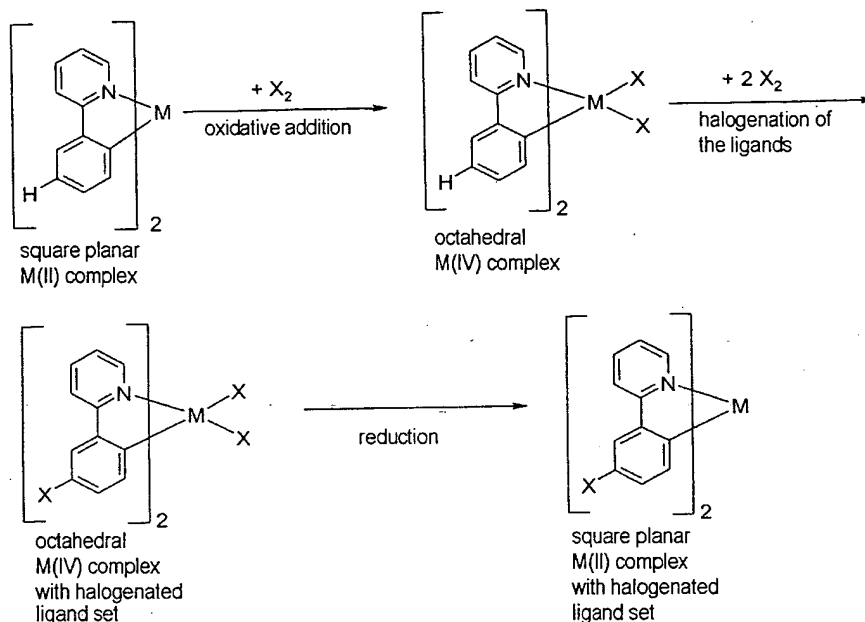
subsequent addition of a reducing agent, or with a halogenating agent consisting of an organic O-halogen compound and a halogen X_2 , in the presence or with subsequent addition of a reducing agent, with suitable selection of the stoichiometric ratio of the appropriate halogenating agent to the compounds (9), (10), (11), (12), (13), (14), (15) or (16) and with suitable selection of the reaction parameters such as reaction temperature, reaction medium, concentration and reaction times, reproducibly in more than 80% yield, without use of chromatographic purification processes, in some cases after recrystallization, in purities of > 99% by NMR or HPLC (see Example 1-3).

The above-described process is notable particularly for several features which have not been described to date in the literature:

1) without wishing to be bound thereby to a particular theory, we suspect that the exceptional tendency of square planar palladium and platinum complexes to the oxidative addition of electrophiles, here of halogens or their analogs which transfer halogenium ions, always has the consequence that a rapid oxidative addition to the metal center occurs initially with consumption of one equivalent of halogen and formation of octahedral dihalopalladium(IV) and -platinum(IV) complexes. In a second, subsequent step, these react with further equivalents of halogen to halogenate the ligands and form octahedral dihalopalladium (IV) and -platinum(IV) complexes with a halogenated, ortho-metalated ligand set. The subsequent reduction of these octahedral dihalopalladium(IV) and -platinum(IV) complexes with a halogenated ortho-metalated ligand set then leads to the square planar palladium(II) and platinum(II) complexes with a correspondingly halogenated ligand set described here. Scheme 1

shows this reaction sequence schematically.

Scheme 1:



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2) The selective 5'-mono- and 5',5''-dihalogenation on square planar palladium(II) and platinum(II) complexes via the above-described dihalo-
 10 palladium(IV) and -platinum(IV) complexes is unexpected and not known in this form. The observed high selectivity is suspected to result from the activation which is experienced by the position para to the palladium or platinum atom as
 15 a result of this atom. The unexpectedly high activity of this position compared to an electrophilic substitution, here halogenation, is utilized selectively by the use of mild halogenating agents.

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3) A crucial factor for the achievement of high selectivities and high reaction rates is frequently, depending on the halogenating agent, working in the presence of an acid-binding agent
 25 which binds hydrohalic acid formed in the course of the substitution. This is a surprising finding,

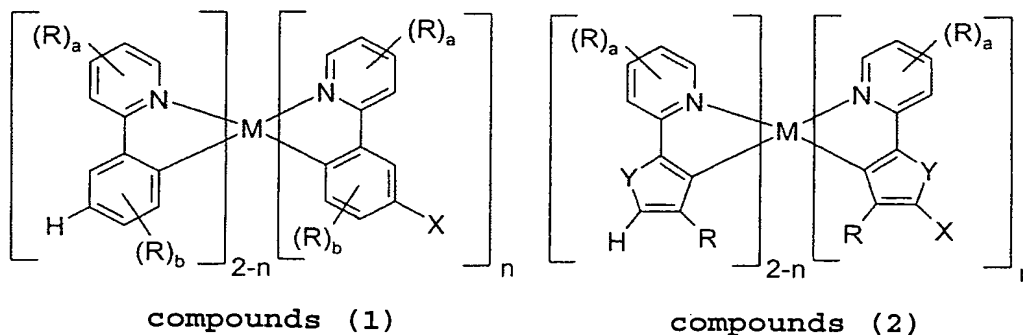
by which the side reactions are apparently suppressed effectively. The inventive halogenating agents accordingly comprise an acid-binding agent, such as a base, which is either an intrinsic part of the halogenating agent or is added additionally to the halogenating agent.

- 4) The high conversion achieved, which is reflected in the reproducibly very good yields of isolated product, is unexpected and unique for the halogenation of ortho-metalated ligands bound to metals of the nickel group.
- 5) The resulting compounds are obtained without costly and inconvenient chromatographic purification, in some cases after recrystallization, in very good purities of > 99% by NMR or HPLC. This is essential for the use in optoelectronic components, and the utilization as valuable intermediates for the preparation of corresponding compounds.

As outlined above, the inventive compounds have not been described before and are thus novel.

The present invention thus provides the compounds (1) and (2) according to scheme 2

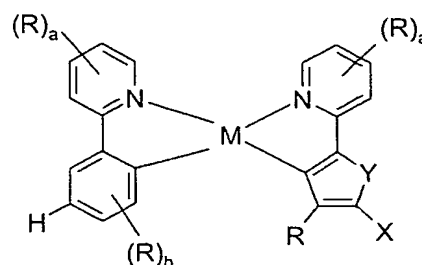
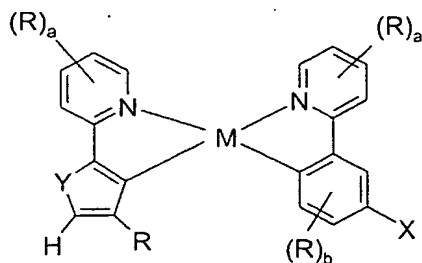
Scheme 2:



where the symbols and indices are each defined as follows:

- M is Pd, Pt;
 X is Cl, Br, I;
 5 Y is O, S, Se, NR¹;
 R is the same or different at each instance and is H, F, Cl, Br, I, NO₂, CN, a straight-chain or branched or cyclic alkyl or alkoxy group having 1 to 20 carbon atoms, in which one or more
 10 nonadjacent CH₂ groups may be replaced by -O-, -SiR¹₂-, -S-, -NR¹- or -CONR¹- and in which one or more hydrogen atoms may be replaced by F, or an aryl or heteroaryl group having from 4 to 14 carbon atoms which may be substituted by one or
 15 more nonaromatic R radicals, and a plurality of R substituents, either on the same ring or on the two different rings, may together in turn form one further aliphatic or aromatic, mono- or polycyclic ring system;
 20 R¹ are the same or different at each instance and are each H or an aliphatic or aromatic hydrocarbon radical having from 1 to 20 carbon atoms;
 a is 0, 1, 2, 3 or 4, preferably 0, 1 or 2;
 b is 0, 1, 2 or 3, preferably 0 or 1;
 25 n is 1 or 2.

A further embodiment of the invention relates to those Pd and Pt complexes which simultaneously have ligands of the type as in compounds (1) and those of compounds
 30 (2), i.e. mixed ligand systems. These are described by the formulae (1a) and (2a):

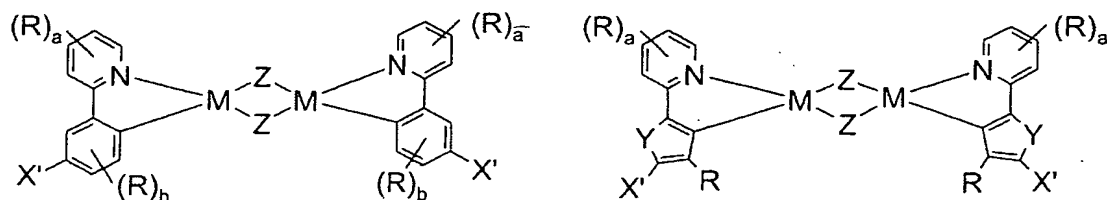


compounds (1a)**compounds (2a)**

where the symbols and indices are each defined under the formulae (1) and (2).

- 5 The present invention likewise provides the compounds (3) and (4) according to scheme 3

Scheme 3:

10 **compounds (3)****compounds (4)**

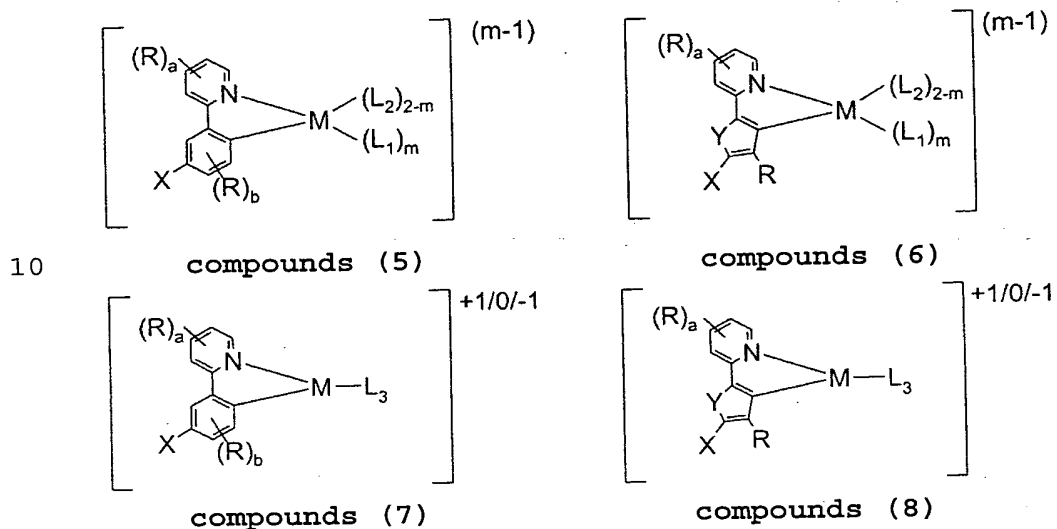
where the symbols and indices are each defined as follows:

- M is Pd, Pt;
- X' is H, Cl, Br or I, with the proviso that at least one X' per formula is selected from Cl, Br or I;
- 15 Y is O, S, Se, NR¹;
- Z is identically F, Cl, Br, I, O-R¹, S-R¹, N(R¹)₂
- R is the same or different at each instance and is H, F, Cl, Br, I, NO₂, CN, a straight-chain or branched or cyclic alkyl or alkoxy group having 1 to 20 carbon atoms, in which one or more nonadjacent CH₂ groups may be replaced by -O-, -SiR¹₂-, -S-, -NR¹- or -CONR¹- and in which one or more hydrogen atoms may be replaced by F, or an aryl or heteroaryl group having from 4 to 14 carbon atoms which may be substituted by one or more nonaromatic R radicals, and a plurality of R substituents, either on the same ring or on the two different rings, may together in turn form one further aliphatic or aromatic, mono- or polycyclic ring system;
- 25 R¹ are the same or different at each instance and are each H or an aliphatic or aromatic hydrocarbon radical having from 1 to 20 carbon atoms;
- 30

- a is 0, 1, 2, 3 or 4, preferably 0, 1 or 2;
 b is 0, 1, 2 or 3, preferably 0 or 1.

The present invention likewise provides the compounds
 5 (5), (6), (7) and (8) according to scheme 4

Scheme 4:



where the symbols and indices are each defined as follows:

- 15 M is Pd, Pt;
 X is Cl, Br, I;
 Y is O, S, Se, NR¹;
 R is the same or different at each instance and is
 20 H, F, Cl, Br, I, NO₂, CN, a straight-chain or
 branched or cyclic alkyl or alkoxy group having 1
 to 20 carbon atoms, in which one or more
 nonadjacent CH₂ groups may be replaced by -O-,
 -SiR¹₂-, -S-, -NR¹- or -CONR¹- and in which one or
 25 more hydrogen atoms may be replaced by F, or an
 aryl or heteroaryl group having from 4 to 14
 carbon atoms which may be substituted by one or
 more nonaromatic R radicals, and a plurality of R
 substituents, either on the same ring or on the
 two different rings, may together in turn form one
 30 further aliphatic or aromatic, mono- or polycyclic
 ring system;

- R^1 are the same or different at each instance and are each H or an aliphatic or aromatic hydrocarbon radical having from 1 to 20 carbon atoms;
- L_1 is an uncharged, monodentate ligand;
- 5 L_2 is a monoanionic, monodentate ligand;
- L_3 is an uncharged or mono- or dianionic bidentate ligand;
- a is 0, 1, 2, 3 or 4, preferably 0, 1 or 2;
- b is 0, 1, 2 or 3, preferably 0 or 1;
- 10 m is 0, 1 or 2.

Inventive uncharged, monodentate ligands L_1 are carbon monoxide, an isonitrile, for example tert-butylisonitrile, cyclohexylisonitrile, adamantyl-
15 isonitrile, an amine, for example trimethylamine, triethylamine, morpholine, phosphines, for example trifluorophosphine, or else aliphatic, aromatic or heteroaromatic phosphines such as trimethylphosphine, tricyclohexylphosphine, dicyclohexylphenylphosphine,
20 tri-o-tolylphosphine, tri-tert-butylphosphine, tri-phenylphosphine, tris(pentafluorophenyl)phosphine, phosphites, for example trimethyl phosphite, triethyl phosphite, arsines, for example trifluoroarsine, trimethylarsine, tricyclohexylarsine, tri-tert-
25 butylarsine, triphenylarsine, tris(pentafluorophenyl)-arsine, stibines, for example trifluorostibine, trimethylstibine, tricyclohexylstibine, tri-tert-butylstibine, triphenylstibine, tris(pentafluorophenyl)stibine or a nitrogen-containing heterocycle,
30 for example pyridine, pyridazine, pyrazine, triazine.

Inventive monoanionic, monodentate ligands L_2 are halides such as F, Cl, Br, I, cyanide, cyanate, isocyanate, thiocyanate, isothiocyanate, alkoxides, for
35 example methoxide, ethoxide, propoxide, isopropoxide, tert-butoxide, phenoxide, a thioalkoxide, in particular, for example, methanethiolate, ethanethiolate, propanethiolate, isopropanethiolate,

tert-thiobutoxide, thiophenoxide, amides, for example dimethylamide, diethylamide, diisopropylamide, carboxylates, for example acetate, trifluoroacetate, propionate, benzoate, and anionic nitrogen-containing
5 heterocycles such as morpholide, pyrrolide, imidazolidine, pyrazolidine.

Inventive uncharged or mono- or dianionic, bidentate ligands L_3 are diamines, for example ethylenediamine,
10 N,N,N',N'-tetramethylethylenediamine, propylenediamine, N,N,N',N'-tetramethylpropylenediamine, cis-, trans-diaminocyclohexane, cis-, trans-N,N,N',N'-tetramethyldiaminocyclohexane, imines, for example 2[(1-(phenylimino)ethyl)pyridine, 2[(1-(2-methylphenyl-
15 imino)ethyl)pyridine, 2[(1-(2,6-diisopropylphenylimino)ethyl)pyridine, 2[(1-methylimino)ethyl)pyridine, 2[(1-(ethylimino)ethyl)pyridine, 2[(1-(isopropylimino)ethyl)pyridine, 2[(1-(tert-butylimino)ethyl)pyridine, diimines, for example 1,2-bis(methylimino)ethane, 1,2-
20 bis(ethylimino)ethane, 1,2-bis(isopropylimino)ethane, 1,2-bis(tert-butylimino)ethane, 2,3-bis(methylimino)butane, 2,3-bis(ethylimino)butane, 2,3-bis(isopropylimino)butane, 2,3-bis(tert-butylimino)butane, 1,2-bis(phenylimino)ethane, 1,2-bis(2-methylphenylimino)ethane,
25 imino)ethane, 1,2-bis(2,6-diisopropylphenylimino)ethane, 1,2-bis(2,6-di-tert-butylphenylimino)ethane, 2,3-bis(phenylimino)butane, 2,3-bis(2-methylphenylimino)butane, 2,3-bis(2,6-diisopropylphenylimino)butane, 2,3-bis(2,6-di-tert-butylphenylimino)butane,
30 heterocycles containing two nitrogen atoms, for example 2,2'-bipyridine, o-phenanthroline, diphosphines, for example bis-diphenylphosphinomethane, bisdiphenylphosphinoethane, bis(diphenylphosphino)propane, bis(dimethylphosphino)methane, bis(dimethylphosphino)ethane,
35 bis(dimethylphosphino)propane, bis(diethylphosphino)methane, bis(diethylphosphino)ethane, bis(diethylphosphino)propane, bis(di-tert-butylphosphino)methane, bis(di-tert-butylphosphino)ethane, bis(tert-butylphosphino)propane, 1,3-diketones derived from

1,3-diketones, for example acetylacetone,
benzoylacetone, 1,5-diphenylacetylacetone,
dibenzoylmethane, bis(1,1,1-trifluoroacetyl)methane,
3-ketonates derived from 3-keto esters, for example
5 ethyl acetoacetate, carboxylates derived from
aminocarboxylic acids, for example pyridine-2-
carboxylic acid, quinoline-2-carboxylic acid, glycine,
dimethylglycine, alanine, dimethylaminoalanine,
salicyliminates derived from salicylimines, in
10 particular, for example, methylsalicylimine,
ethylsalicylimine, phenylsalicylimine, dialkoxides
derived from dialcohols, in particular, for example,
ethylene glycol, 1,3-propylene glycol, dithiolates
derived from dithiols, for example 1,2-ethylenedithiol,
15 1,3-propylenedithiol, or heteroarylborates, for example
tetrakis(1-imidazolyl)borate, tetrakis(1-pyrazolyl)-
borate.

The inventive complexes (1) to (8) and (1a) and (2a)
20 have the following advantages over the prior art:

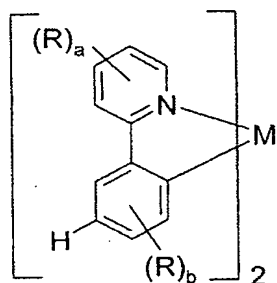
- 1) As a result of the functionalization, it is simple
to covalently incorporate these complexes as
(co)monomers, for example, into corresponding
polymers or oligomers. This may be effected either
25 in the main chain or at the end of the main chain,
or, in the case of appropriate further reactions,
into the side chain of the polymer.
- 2) It is possible analogously by appropriate
reactions to provide "defined low molecular weight
30 complexes" which, however, have specific
properties (for example high solubility, low
tendency to crystallize). The incorporation into
defined oligomers (for example dendrimers) is also
possible effortlessly by the same reactions.
- 35 3) The access, outlined under 1) and 2), to
corresponding functionalizations is of very high
significance, since it is very important to
integrate metal complexes either into polymers or
into readily soluble low molecular weight

substances.

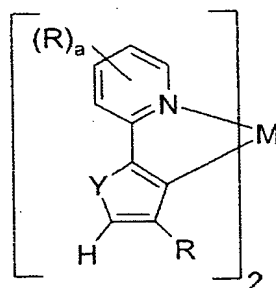
- 4) It is likewise advantageous that the claimed complexes can be prepared in good purity and high yield. This is of enormous significance firstly for corresponding applications (further processing for use in electrical or electronic devices, for example OLED- or PLED-based displays) and also commercially (owing to the high raw material cost).

The present invention further provides processes for preparing the compounds (1), (2), (3), (4), (5), (6), (7) and (8) by reacting the compounds (9), (10), (11), (12), (13), (14), (15) and (16) according to scheme 5

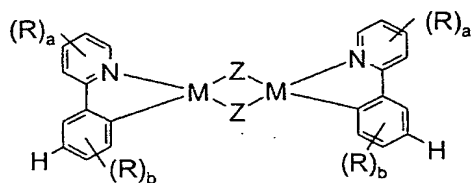
Scheme 5:



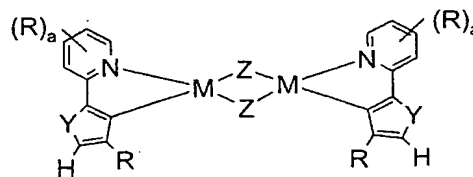
compounds (9)



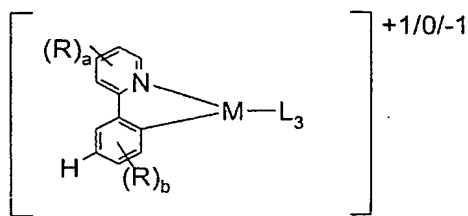
compounds (10)



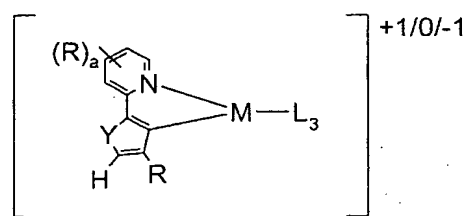
compounds (11)



compounds (12)



compounds (15)



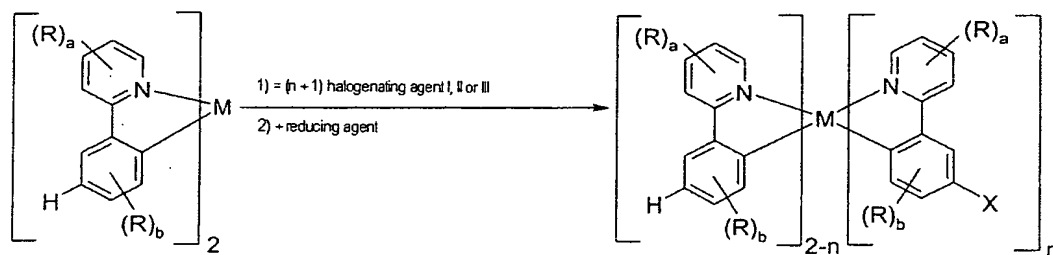
compounds (16)

in which M and the radicals and indices X, Y, Z, R, R¹,

L_1 , L_2 , L_3 , a , b and m are each as defined above with halogenating agents, followed by reducing agents.

The process according to the invention is illustrated
5 by scheme 6:

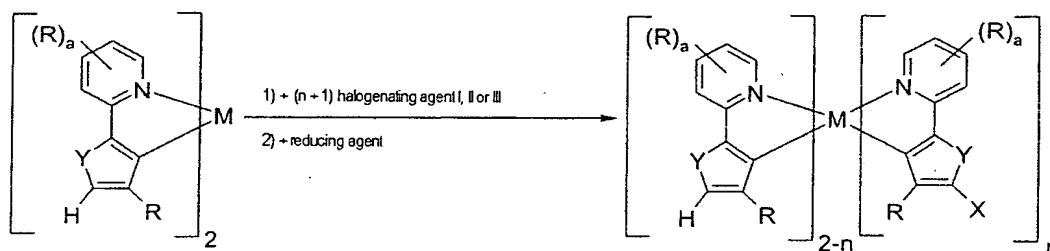
Scheme 6:



compounds (9)

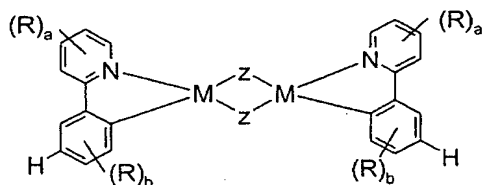
compounds (1)

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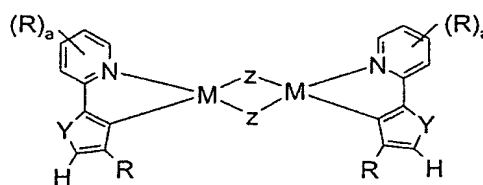


Compounds (10)

compounds (2)

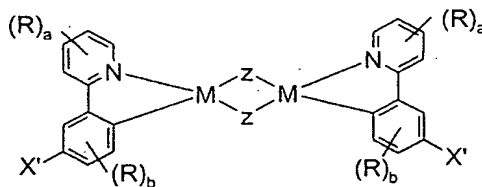


compounds (11)

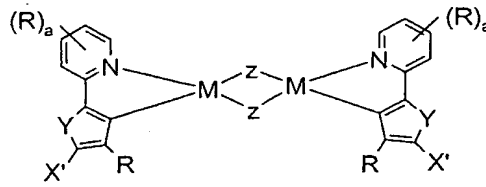


compounds (12)

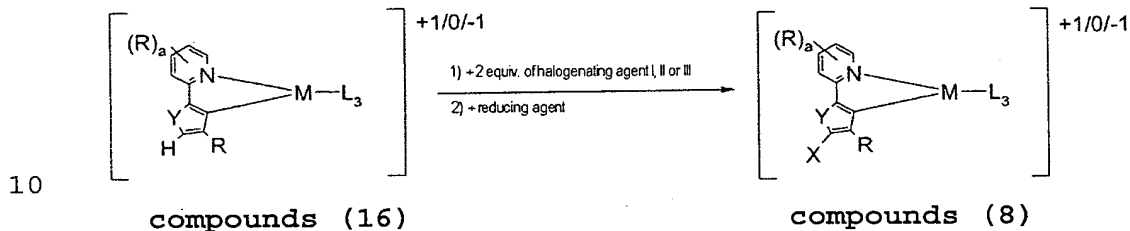
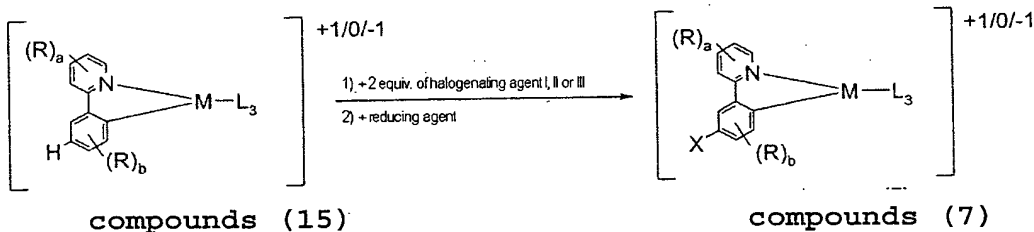
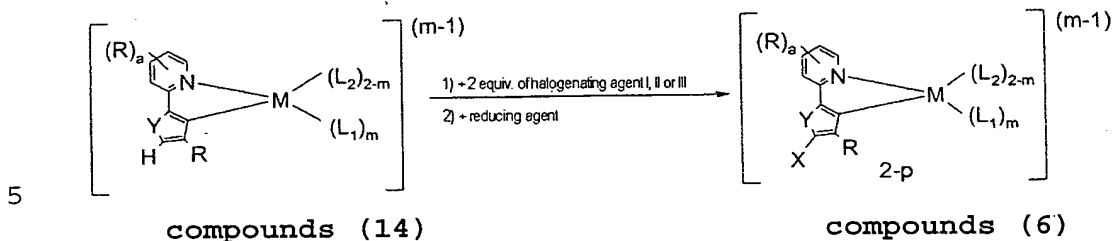
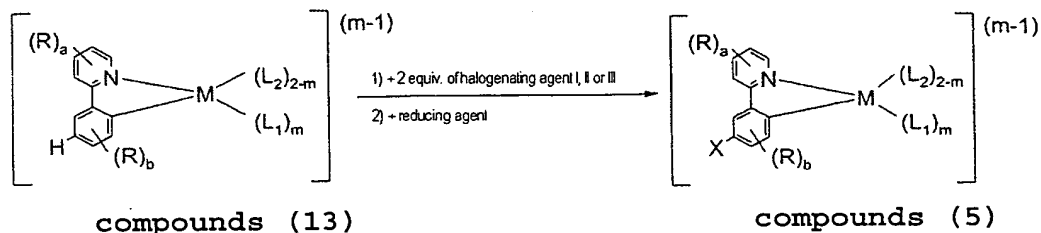
1) + 2 or 3 equiv. of halogenating agent I, II or III
2) + reducing agent



compounds (3)



compounds (4)



The compounds (1a) and (2a) may also be prepared analogously.

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Inventive halogenating agents are the halogens X_2 and the interhalogens $X-X$ and a base in a molar ratio of from 1:1 to 1:100 and optionally a Lewis acid in a molar ratio (halogen to Lewis acid) of from 1:0.1 to 1:0.0001, for example chlorine, bromine or iodine, or chlorine fluoride, bromine fluoride, iodine fluoride, bromine chloride, iodine chloride or iodine bromide, in combination with organic bases such as amines, for example triethylamine, tri-n-butylamine, diisopropyl-
 20 ethylamine, morpholine, N-methylmorpholine and
 25

pyridine, or salts of carboxylic acids such as sodium acetate, sodium propionate, sodium benzoate, or inorganic bases such as sodium phosphate or potassium phosphate or sodium hydrogenphosphate or potassium hydrogenphosphate, sodium hydrogencarbonate or potassium hydrogencarbonate, sodium carbonate or potassium carbonate, or else organic bromine complexes such as pyridinium perbromide, in each case optionally in combination with a Lewis acid, for example boron trifluoride, boron trifluoride etherate, boron trichloride, boron tribromide, boron triiodide, aluminum trichloride, aluminum tribromide, aluminum triiodide, iron(III) chloride, iron(III) bromide, zinc(II) chloride, zinc(II) bromide, tin(IV) chloride, tin(IV) bromide, phosphorus pentachloride, arsenic pentachloride and antimony pentachloride.

These halogenating agents are referred to below as halogenating agents (I).

Further inventive halogenating agents are organic N-halogen compounds, N-halocarboxamides, for example N-chloro-, N-bromo- and N-iodoacetamide, N-chloro-, N-bromo- and N-iodopropionamide, N-chloro-, N-bromo- and N-iodobenzamide, or N-halocarboximides, for example N-chloro-, N-bromo- and N-iodosuccinimide, N-chloro-, N-bromo- and N-iodophthalimide, or N-dihalosulfonamides such as N,N-dibromobenzenesulfonamide, or N-halosulfonamide salts such as chloramine B or T.

These halogenating agents are referred to below as halogenating agents (II). In the case of the halogenating agents (II), the additive use of Lewis acids, as are listed above, for example, may likewise be advantageous.

In the case of the halogenating agents (II), the additive use of Brønsted acids, for example hydrochloric acid, hydrobromic acid, hydriodic acid, sulfuric acid or phosphoric acid, may likewise be advantageous.

Still further inventive halogenating agents are organic O-Hal compounds and halogens X_2 in a molar ratio of from 0.5:1 to 1:1, such as iodoaryl dicarboxylates in a molar ratio of from 0.5:1 to 1:1 with a halogen X_2 , for example iodobenzene diacetate or bistrifluoroacetoxyiodobenzene and elemental bromine in a molar ratio of from 0.5:1 to 1:1, or iodobenzene diacetate or bistrifluoroacetoxyiodobenzene and elemental iodine in a molar ratio of from 0.5:1 to 1:1.

These halogenating agents are referred to below as halogenating agents (III).

In the process according to the invention, a stoichiometric ratio of the halogenating agents (I), (II) or (III), based on the content of active halogen, to the compounds (9), (10), (11), (12), (13), (14), (15) or (16) of 2:1 leads selectively to the compounds (1), (2) where $n = 1$, (3), (4) where one X' is H and the other is halogen, and to the compounds (5), (6), (7) or (8). This is a surprising and unforeseeable result.

In the process according to the invention, a stoichiometric ratio of the halogenating agents (I), (II) or (III), based on the content of active halogen, to the compounds (9), (10), (11) or (12) of from 3:1 to 1000:1 leads selectively to the compounds (1), (2) where $n = 2$, or (3), (4) where both of X' are halogen. This is a surprising and unforeseeable result.

The stoichiometric ratios described here are preferred embodiments of the present invention since they lead to uniformly substituted products. It is self-evident that slight deviations from the abovementioned ratios still lead to good to acceptable results.

According to the invention, a reducing agent is added to the reaction mixture in a molar ratio of from 1:1 to 10 000:1 based on the compounds (9), (10), (11), (12),

(13), (14), (15) or (16). The addition may be effected either simultaneously with the addition of the halogenating agents (I), (II) or (III), or preferably after a time delay.

5

Inventive reducing agents are hydrazine (hydrate) or salts thereof, for example hydrazine hydrochloride, hydrobromide, hydroiodide, hydrazine sulfate, hydrazine nitrate and hydrazine phosphate, hydroxylamine or salts thereof, for example hydroxylamine hydrochloride, hydrobromide, hydroiodide, hydroxylamine nitrate, hydroxylamine phosphate and hydroxylamine sulfate, hydroxylamine-O-sulfonic acid and hydroquinones, for example hydroquinone or tetramethylhydroquinone, alkali metal and alkaline earth metal sulfites such as lithium, sodium, potassium and magnesium sulfite, alkali metal and alkaline earth metal dithionites, for example lithium, sodium, potassium and magnesium dithionite, alkali metals and alkaline earth metals, for example lithium, sodium, potassium and magnesium, calcium, barium, and their amalgams and other corresponding alloys, transition metals such as manganese, iron, nickel and zinc, and transition metal alloys, for example Raney nickel.

25

According to the invention, the reduction may also be effected by dry-heating, under reduced pressure, the palladium(IV) or platinum(VI) compounds which have been formed as intermediates and isolated in substance.

30

Inventive reaction media are protic or aprotic, halogen-free or halogenated solvents, for example alcohols such as methanol, ethanol, propanol, butanol, polyhydric alcohols such as ethylene glycol or propylene glycol, nitriles such as acetonitrile, propionitrile or benzonitrile, ethers such as diethyl ether, THF or dioxane, aromatic hydrocarbons such as benzonitrile, nitrobenzene or chlorobenzene, N,N-dialkylamides such as dimethylformamide, dimethyl-

acetamide or N-methylpyrrolidone, sulfoxides such as dimethyl sulfoxide, sulfones such as dimethylsulfone or sulfolane, halogenated hydrocarbons such as dichloromethane, trichloromethane, 1,1-dichloroethane, 1,2-dichloroethane, 1,1,2,2-tetrachloroethane; preference is given to aromatic or chlorinated solvents.

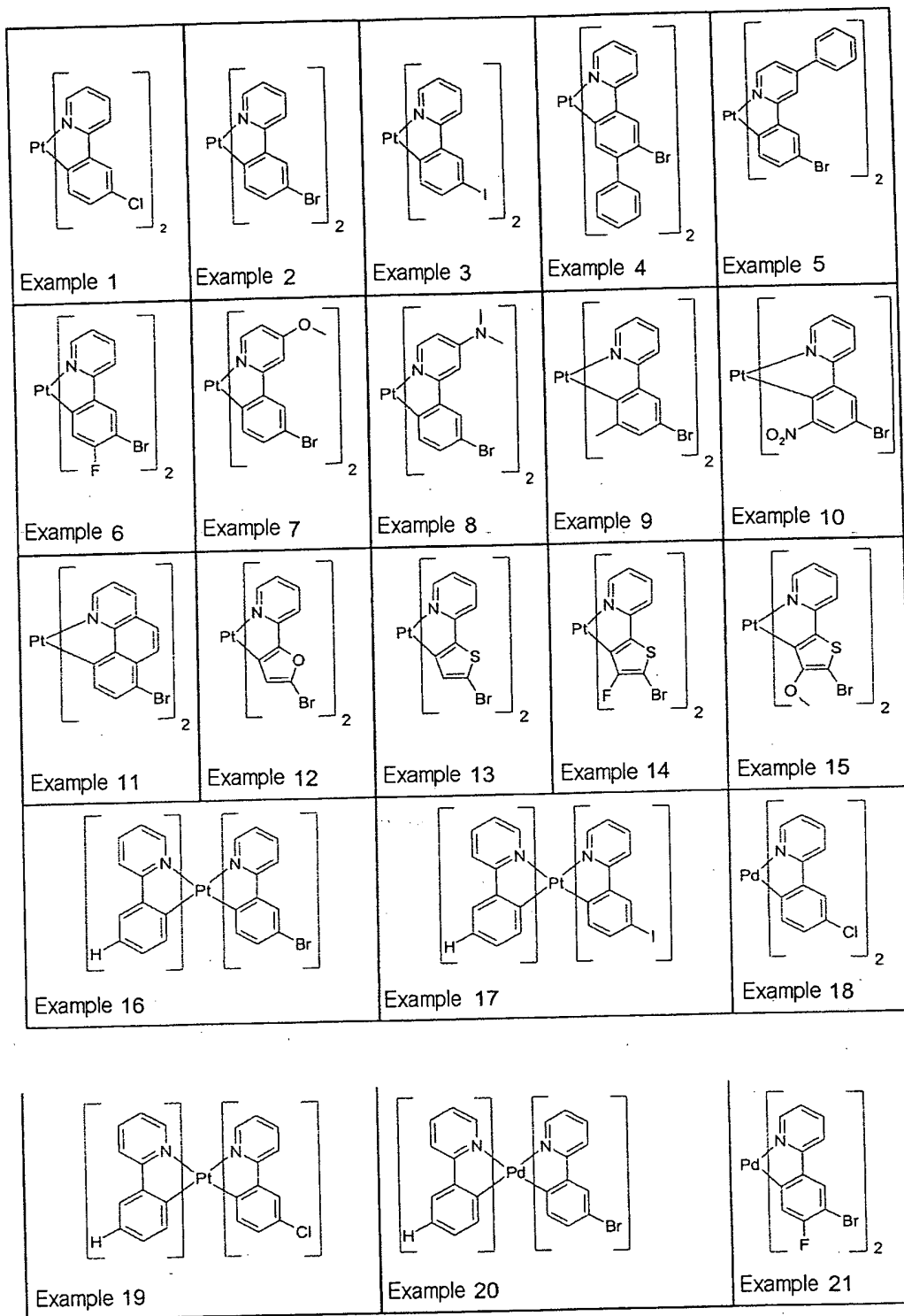
According to the invention, the reaction is carried out within the temperature range from -78°C to 150°C, preferably from 0°C to 100°C, very preferably from 10°C to 60°C.

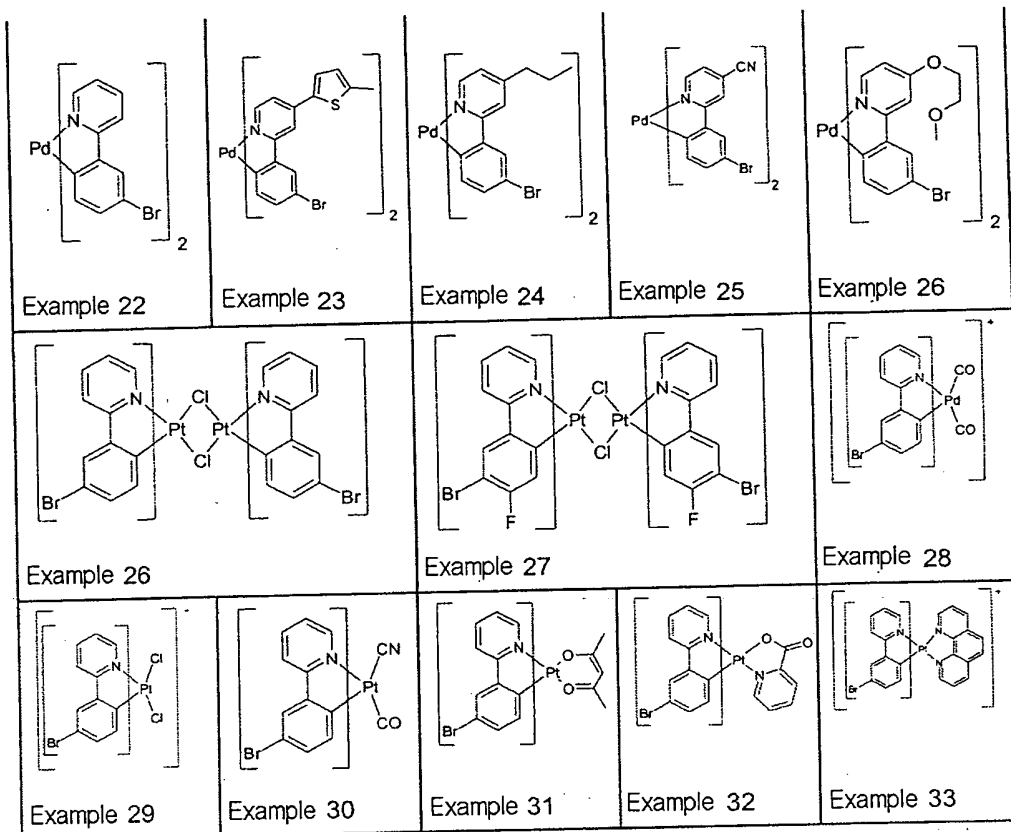
According to the invention, the concentration of the palladium-containing or platinum-containing reactants, compounds (9), (10), (11), (12), (13), (14), (15) or (16), is in the range from 0.0005 mol/l to 2 mol/l, more preferably in the range from 0.002 mol/l to 0.1 mol/l.

According to the invention, the palladium-containing or platinum-containing reactants may be present dissolved or suspended in the reaction medium.

According to the invention, the reaction is carried out within from 10 minutes up to 100 hours, preferably within from 1 h to 40 h.

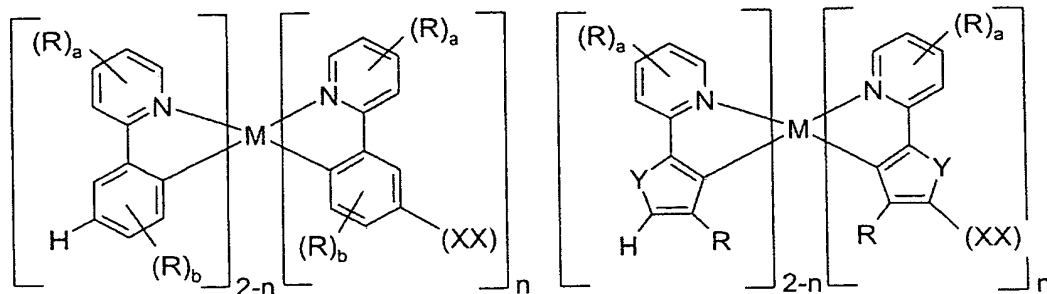
It is possible with the synthetic methods illustrated here to prepare the compounds (1), (1a), (2), (2a), (3), (4), (5), (6), (7) or (8), including the examples shown below.





The thus obtained inventive compounds may find use, for example, as comonomers to obtain corresponding conjugated or else semiconjugated or nonconjugated polymers. The corresponding copolymerization is preferably effected via the halogen functionality. It is thus possible to copolymerize them into polymers including soluble polyfluorenes (for example according to EP-A-842 208 or WO 00/22026), polyspirobifluorenes (for example according to EP-A-707 020 or EP-A-894 107), poly-para-phenylenes (for example according to WO 92/18552), polycarbazoles or else polythiophenes (for example according to EP-A-1 028 136).

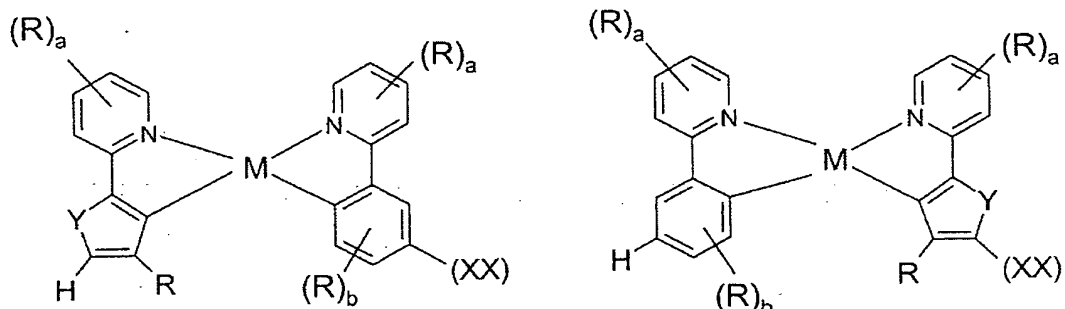
The invention therefore further provides conjugated or semiconjugated and nonconjugated polymers containing one or more compounds of the formula (1') and/or (2')



compounds (1')

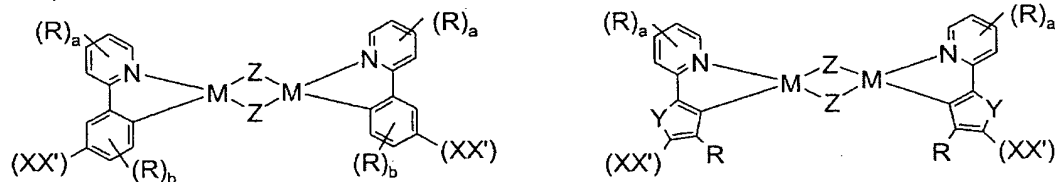
compounds (2')

and/or of the formula (1a') and/or (2a')



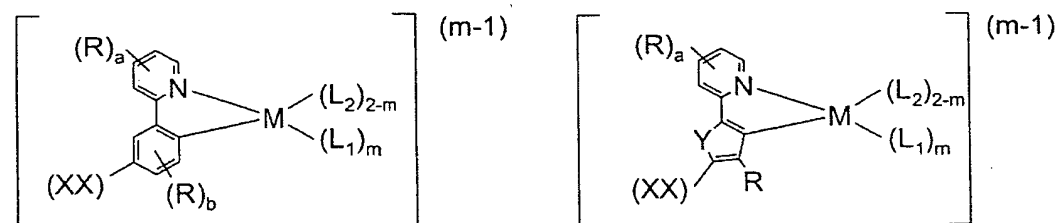
5 compounds (1a')

compounds (2a')

and/or of the formula (3'), (4'), (5'), (6'), (7')
and/or (8')

compounds (3')

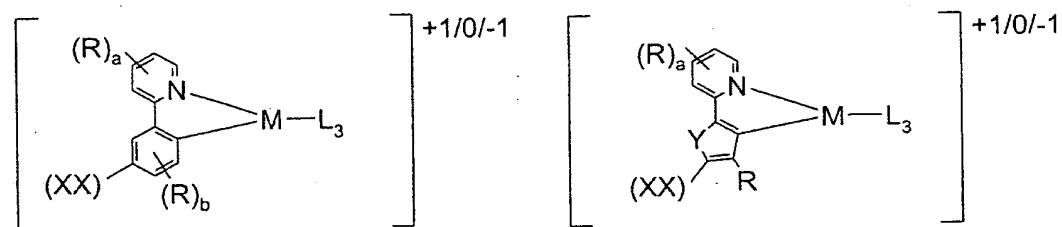
compounds (4')



10

compounds (5')

compounds (6')



compounds (7')

compounds (8')

where the symbols and indices are each defined as follows:

- M is Pd, Pt;
- Y is O, S, Se, NR¹;
- 5 R is the same or different at each instance and is H, F, Cl, Br, I, NO₂, CN, a straight-chain or branched or cyclic alkyl or alkoxy group having 1 to 20 carbon atoms, in which one or more nonadjacent CH₂ groups may be replaced by -O-,
10 -SiR¹₂-, -S-, -NR¹- or -CONR¹- and in which one or more hydrogen atoms may be replaced by F, or an aryl or heteroaryl group having from 4 to 14 carbon atoms which may be substituted by one or more nonaromatic R radicals, and a plurality of R
15 substituents, either on the same ring or on the two different rings, may together in turn form one further aliphatic or aromatic, mono- or polycyclic ring system;
- R¹ are the same or different at each instance and are
20 each H or an aliphatic or aromatic hydrocarbon radical having from 1 to 20 carbon atoms;
- L₁ is an uncharged, monodentate ligand;
- L₂ is a monoanionic, monodentate ligand;
- L₃ is an uncharged or mono- or dianionic bidentate
25 ligand;
- a is 0, 1, 2, 3 or 4;
- b is 0, 1, 2 or 3;
- m is 0, 1 or 2;
- n is 1 or 2;
- 30 (XX) is a bond to the conjugated or semiconjugated or nonconjugated polymer;
- (XX') is H or a bond to the conjugated or semiconjugated or nonconjugated polymer, but at least one (XX') per formula is a bond to the
35 conjugated or semiconjugated or nonconjugated polymer.

Preference is given to conjugated, semiconjugated or nonconjugated polymers which have been obtained using

one or more compounds of the formula (1), (1a), (2), (2a) and/or (3) to (8).

5 Conjugated or semiconjugated polymers refer to polyfluorenes, polyspirobifluorenes, poly-para-phenylenes, polycarbazoles or polythiophenes.

The conjugated or semiconjugated polymers based on polyfluorenes are preferably the polyfluorenes
10 disclosed in EP-A-842 208 and WO 00/22026.

The conjugated or semiconjugated polymers based on polyspirobifluorenes are preferably the polyspirobifluorenes disclosed in EP-A-707 020 and
15 EP-A-894 107.

The conjugated or semiconjugated polymers based on poly-para-phenylenes are preferably the poly-para-phenylenes disclosed in WO 92/18552.
20

The conjugated or semiconjugated polymers based on polythiophenes are preferably the polythiophenes disclosed in EP-A-1 028 136.

25 In addition, the inventive compounds may also be functionalized further by the abovementioned reaction types, for example, and thus converted to extended low molecular weight Pd or Pt complexes or defined oligomers (for example dendrimers). An example to be
30 mentioned here is the functionalization with arylboronic acids according to Suzuki or with amines according to Hartwig-Buchwald.

The halogenated complexes or the polymers or else "extended low molecular weight complexes" or else the
35 defined oligomers obtained therefrom may be used in electrical or electronic components, for example as light-emitting materials in organic or polymeric light-emitting diodes (OLEDs or PLEDs). However, other applications, for example in organic solar cells,

organic lasers, organic photodetectors, and the like are also conceivable.

The invention therefore also provides electronic components, for example organic or polymeric light-emitting diodes (OLEDs or PLEDs), organic integrated circuits (O-ICs), organic field-effect transistors (O-FETs), organic thin-film transistors (O-TFTs), organic solar cells (O-SCs) or organic laser diodes (O-lasers), comprising one or more inventive halogenated palladium or platinum complexes or one or more inventive polymers which have been obtained using these inventive palladium or platinum complexes.

The present invention is illustrated in detail by the examples which follow, without any intention that it be restricted thereto. Those skilled in the art can prepare further inventive complexes from the descriptions without inventive activity, and employ the process according to the invention.

Examples

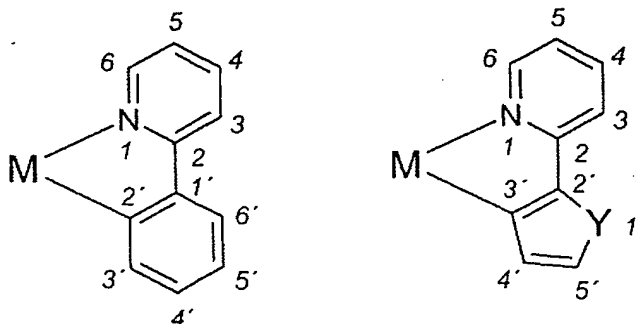
Synthesis of symmetrically and asymmetrically functionalized bis-ortho-metalated organopalladium or organoplatinum compounds:

The syntheses which follow have, unless stated otherwise, been carried out under air using commercial solvents. The reactants were purchased from Aldrich [N-chlorosuccinimide, N-bromosuccinimide, HCl, HBr, hydrazine hydrate]. Before the N-haloimides were used, the content of active halogen was determined iodometrically [analogously to: K.W. Rosenmund, W. Kuhnenn, Ber. 1923, 56, 1262]. Bis[2-(2-pyridinyl-κN)phenyl-κC}platinum was prepared by literature methods (L. Chassot, E. Müller, A. Zelewsky, Inorg. Chem. 1984, 23, 4249-4253).

Numbering scheme for the assignment of the ¹H NMR signals [analogously to: C. Coudret, S. Fraysse, J.-P-

Launay, Chem. Commun., 1998, 663-664]:

Scheme 7:



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Example 1: Bis[2-(2-pyridinyl-κN)(5-chlorophenyl)-κC]platinum(II)

588 mg (4.4 mmol) of N-chlorosuccinimide and 200 μl of conc. HCl were added under exclusion of light to an efficiently stirred solution of 504 mg (1.0 mmol) of bis[2-(2-pyridinyl-κN)phenyl-κC]platinum(II) in 200 ml of dichloromethane. The reaction mixture was stirred at room temperature for a further 20 h. Subsequently, 240 μl (5 mmol) of hydrazine hydrate and 100 ml of ethanol were added, and the mixture was heated under reflux for 2 h. After concentration to a volume of 20 ml under reduced pressure, the solution was admixed with 200 ml of ethanol. Subsequently, the microcrystalline precipitate was filtered off (P4), washed three times with 20 ml of ethanol and then dried under reduced pressure (60°C, 10⁻⁴ bar). The yield, at a purity of > 99.5% by ¹H NMR, was 501 mg, corresponding to 87.5%.

¹H NMR (CD₂Cl₂): [ppm] = 8.91 (m, 3H), 7.91 (m, 3H), 7.83 (m, 3H), 7.57 (m, 3H), 7.43 (m, 3H), 7.37 (m, 3H), 7.09 (m, 3H).

Example 2: Bis[2-(2-pyridinyl-κN)(5-bromophenyl)-κC]platinum(II)

783 mg (4.4 mmol) of N-bromosuccinimide and 170 μl of 48% by weight HBr were added under exclusion of light to an efficiently stirred solution of 504 mg (1.0 mmol) of bis[2-(2-pyridinyl-κN)phenyl-κC]platinum(II) in

30

200 ml of dichloromethane. The reaction mixture was stirred at room temperature for a further 20 h. Subsequently, 240 μ l (5 mmol) of hydrazine hydrate and 100 ml of ethanol were added, and the mixture was heated under reflux for 2 h. After concentration to a volume of 20 ml under reduced pressure, the solution was admixed with 200 ml of ethanol. Subsequently, the microcrystalline precipitate was filtered off (P4), washed three times with 20 ml of ethanol and then dried under reduced pressure (60°C, 10^{-4} mbar). The yield, at a purity of > 99.5% by ^1H NMR, was 613 mg, corresponding to 92.7%.

^1H NMR (DMSO- d_6): [ppm] = 8.85 (m, 3H), 7.93 (m, 3H), 7.78 (m, 3H), 7.52 (m, 3H), 7.39 (m, 3H), 7.35 (m, 3H), 7.02 (m, 3H).

Example 3: Bis[2-(2-pyridinyl- κN)(5-bromophenyl- κC)platinum(II)]

783 mg (4.4 mmol) of N-bromosuccinimide and 170 μ l of 48% by weight HBr were added under exclusion of light to an efficiently stirred solution of 504 mg (1.0 mmol) of bis[2-(2-pyridinyl- κN)phenyl- κC]platinum(II) in 200 ml of dichloromethane. The reaction mixture was stirred at room temperature for a further 20 h. After concentration to a volume of 20 ml under reduced pressure, the solution was admixed with 200 ml of ethanol. Subsequently, the microcrystalline precipitate was filtered off (P4), washed three times with 20 ml of ethanol and then dried under reduced pressure (60°C, 10^{-4} mbar). The thus obtained platinum(IV) compound was sublimed at a temperature of from 380 to 410°C under reduced pressure (approx. $5 \cdot 10^{-4}$ mbar), in the course of which the product (the desired platinum(II) compound) was obtained as the sublimate. The yield, at a purity of > 99.5% by ^1H NMR, was 569 mg, corresponding to 86.0%.

^1H NMR (DMSO- d_6): [ppm] = 8.85 (m, 3H), 7.93 (m, 3H), 7.78 (m, 3H), 7.52 (m, 3H), 7.39 (m, 3H), 7.35 (m, 3H), 7.02 (m, 3H).